

RiO5 METHOD (15)

ERL-ECU/LM/0005

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^{210}Po and ^{210}Pb — Co-APDC chelate co-precipitation

— Seawater samples

^{210}Po and ^{210}Pb radiochemistry in seawater samples

Co-APDC chelate co-precipitation method based on Fler and Bacon (1984) and modified with own tests at UAB

Disclaimer

It is the responsibility of the analyst to follow established safety and health practices. Although each laboratory identified as the source has tested the methods, each user should perform an individual validation procedure.

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1 SCOPE

This method specifies the minimum requirements and laboratory methods for the analysis of total ^{210}Pb and ^{210}Po in seawater samples.

Samples are collected in acid-cleaned containers and pretreated on board, by acidifying and co-precipitating the samples. Post processing will take place at the home laboratory by auto-plating of Po isotopes onto silver disks on a 1 M HCl solution. Po isotopes emissions are measured by alpha spectrometry. Isotope ingrowth and decay corrections are applied to calculate the ^{210}Po and ^{210}Pb activities (see Rigaud et al., 2013).

2 EQUIPMENT and CHEMICAL REAGENTS

2.1 Equipment

- Plastic containers
- Stainless steel filter plates (142 mm)
- Membrane filters (mixed cellulose ester; 0.2 μm pore; 142 mm diameter)
- Peristaltic pump
- Standard laboratory equipment
- Plastic columns (BioRad)
- Glass beakers
- Analytical balance with an accuracy of ± 0.1 mg
- Hot plate
- Hot plate with magnetic stirrer
- Alpha spectrometry system
- Urethane seal coat
- Plastic vials for ICP-OES

2.2 Tracers

- ^{209}Po (0.4 Bq mL^{-1})
- Stable Pb (free of ^{210}Pb) (20 mg mL^{-1})

2.3 Chemical reagents

- Hydrochloric acid (HCl)
- Nitric acid (HNO_3)
- Anion exchange resin (DOWEX-1-X8 or AG 1-X8)

2.4 Solutions

- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (1 g Co/L).
- 2 g/100 mL APDC solution
- 1 M, 2 M, 9 M HCl

3 PROCEDURE

1. Collect 5-10 L seawater samples. Weight them or use calibrated containers.
2. Add concentrated HCl until $\text{pH} < 2$ (1 mL HCl per 1 L of sample).
3. Shake vigorously to homogenize.
4. Spike the samples with a known amount of ^{209}Po (with a 0.4 Bq/mL ^{209}Po solution we add 75 μL) using a calibrated micropipette.
5. Add a known amount of stable Pb (ideally use old lead to minimize contamination; with a 20 mg/mL solution of stable Pb we add 200 μL) using a calibrated micropipette.
6. Shake vigorously to facilitate isotope equilibration. Allow equilibration for ~ 12 h.
7. Add 10 mL of a $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (1 g Co/L).
8. Add 40 mL of a 2 g/100 mL APDC solution.
9. Shake vigorously to facilitate coagulation.
10. Allow a few hours (6 h).
11. Filter the sample through a 0.2 μm membrane filter (142 mm diameter, mixed cellulose ester membrane filter).
12. Rinse the container with 2 M HCl.
13. Place the filter on a falcon tube until further analyses.
14. The filter support can also have some precipitate. Try to rinse it with 2 M HCl and keep the liquid in the falcon tube together with the filter.

This first part usually takes place at sea, the following steps are usually done at the land laboratory.

15. Place the filter on a beaker that has been previously weighted and the weight has been recorded, and add ~ 6 mL of conc. HNO_3 (try to have the filter as submerged in the acid as possible). If there was liquid from the rinsing, transfer that liquid into the beaker and evaporate prior to adding the filter and the concentrated HNO_3 .
16. Once the filter is mostly under HNO_3 , cover the beaker with a watch glass and heat it up.
17. Let it stay until the entire filter is dissolved. If necessary, add more HNO_3 .
18. Once the filter is dissolved, evaporate the sample to dryness.
19. Add 2 mL conc. HCl and evaporate to dryness again (avoid boiling the sample).

20. Repeat the previous step 2 times more.
21. Reconstruct the sample by adding ~80 mL of 1 M HCl.
22. Weight the beaker with the sample and annotate the weight to obtain the weight of the sample.
23. Add a stirring magnet and cover the beaker with a glass watch. Stir the sample on a stirring plate.
24. When the sample is well homogenized, extract an aliquot of 0.4 g on a vial and add Milli-Q until the total weight of the sample is ~10 g. This aliquot will be used to obtain the Pb recovery (expected Pb concentration is ~2 ppm, considering amount of stable Pb added in step 5). The sample is then analyzed by ICP-OES.
25. Place a silver disc, with only one of the sides available for auto-deposition¹, in the sample using a nylon string. Auto-deposition of polonium onto silver discs is used to separate ²¹⁰Po and ²¹⁰Pb.
26. Add a magnet in the sample and place the beaker in a stirring plate.
27. Cover the beaker with a glass watch and heat it to 80°C while stirring it. Leave it for 4-6 h.
28. Get the silver disc, rinse it with Milli-Q water and let it dry before measuring it for alpha spectrometry.
29. Solutions are re-plated, this time the silver disc does not need to be lacquered, thereby providing as much active surface area as possible for auto-deposition of the remaining polonium.
30. Pass solution through an anion exchange resin (DOWEX-1-X8 or AG 1-X8)² to ensure complete elimination of polonium from samples. Collect the sample on a bottle that can be properly sealed and will resist strong acid (9 M HCl).
31. Store for 6-9 months for later determination of ²¹⁰Pb via ²¹⁰Po in-growth.
32. After allowing ²¹⁰Po in-growth, samples are transferred to a glass beaker (pre-weighted) and evaporated to dryness (avoid boiling the sample).
33. Repeat steps 19-28.
34. ²¹⁰Pb and ²¹⁰Po activities at sampling time can then be calculated applying in-growth, decay and recovery corrections following Rigaud et al., (2013).

¹ Add clear urethane seal coat on one side of the silver disc so that polonium can only be deposited onto the other side, optimizing the counting statistics of the sample given that the alpha detector can only measure one side of the disc at a time.

² See section “Column Chemistry to Separate Pb and Po”

Column Chemistry to Separate Pb and Po

1. Dry the plated sample solution completely on a hot plate; some residue might be evident.
2. Add 5 mL conc. HCl and dry completely again; much less or no residue should remain.
3. Add 5 mL 9 M HCl to the sample.
4. Prepare a 9 M HCl anion exchange column as follows. Take ~6 mL of anion exchange resin (DOWEX-1-X8 or AG 1-X8) and load a column. Rinse by passing through 20 mL of deionized water. Condition by adding 5 column volumes (=5 x 6 mL = 30 mL) of 9 M HCl through the column and discard the solution.
5. Transfer the sample solution from (3) to the column. Collect the effluent in a clean beaker or plastic bottle (e.g. 50-100 mL CPE).
6. Rinse the column with 30 mL more of 9 M HCl and collect the combined effluents in the same beaker/bottle. Only the Pb passes and Po is retained.
7. Re-spike the solution at this time with a known amount of ^{209}Po and store solution for in-growth of ^{210}Po for at least 1-2 half-lives.

4 REFERENCES

Rigaud *et al.*, (2013), A methods assessment and recommendations for improving calculations and reducing uncertainties in the determination of ^{210}Po and ^{210}Pb activities in seawater. *Limnology and Oceanography: Methods 11*, pp. 561-571.

Fleer, A. P., and M. P. Bacon (1984), Determination of ^{210}Pb and ^{210}Po in seawater and marine particulate matter, *Nucl. Instruments Methods Phys. Res.*, 223(2-3), 243-249, doi:10.1016/0167-5087(84)90655-0.

5 FLOW CHART

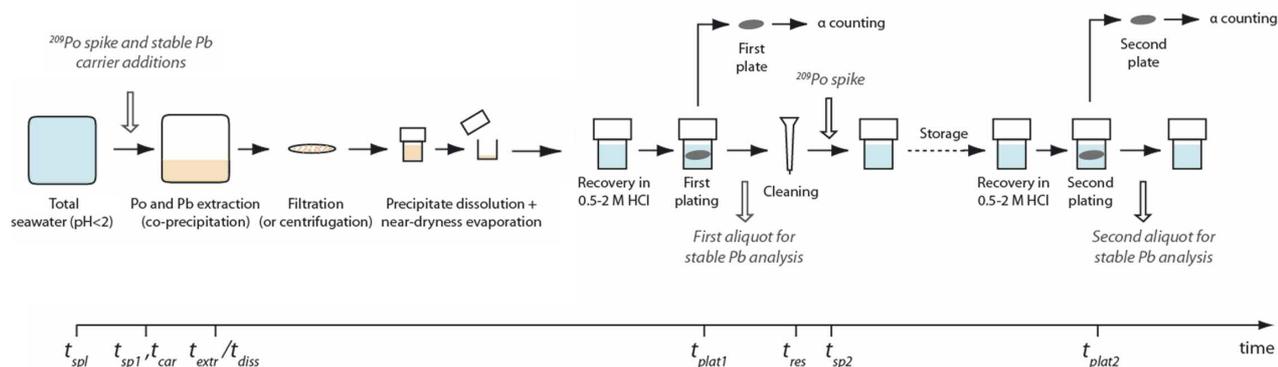


Figure 1: Sample processing scheme for the determination of total ^{210}Po and ^{210}Pb activities. The times term (t) required for each step used in the calculation are provided (see Rigaud et al. 2013). Figure adapted from Rigaud et al. (2013).

6 IMAGES



Image 1: Samples containing the Co-APDC precipitate (see the yellow-greenish color of the samples).



Image 2: Filtering the Co-APDC precipitate (right container) through the membrane filter placed on the filter plate using a peristaltic pump. The filtrated (pH <2) is collected on a “waste” container (left container).



Image 3: Plating.

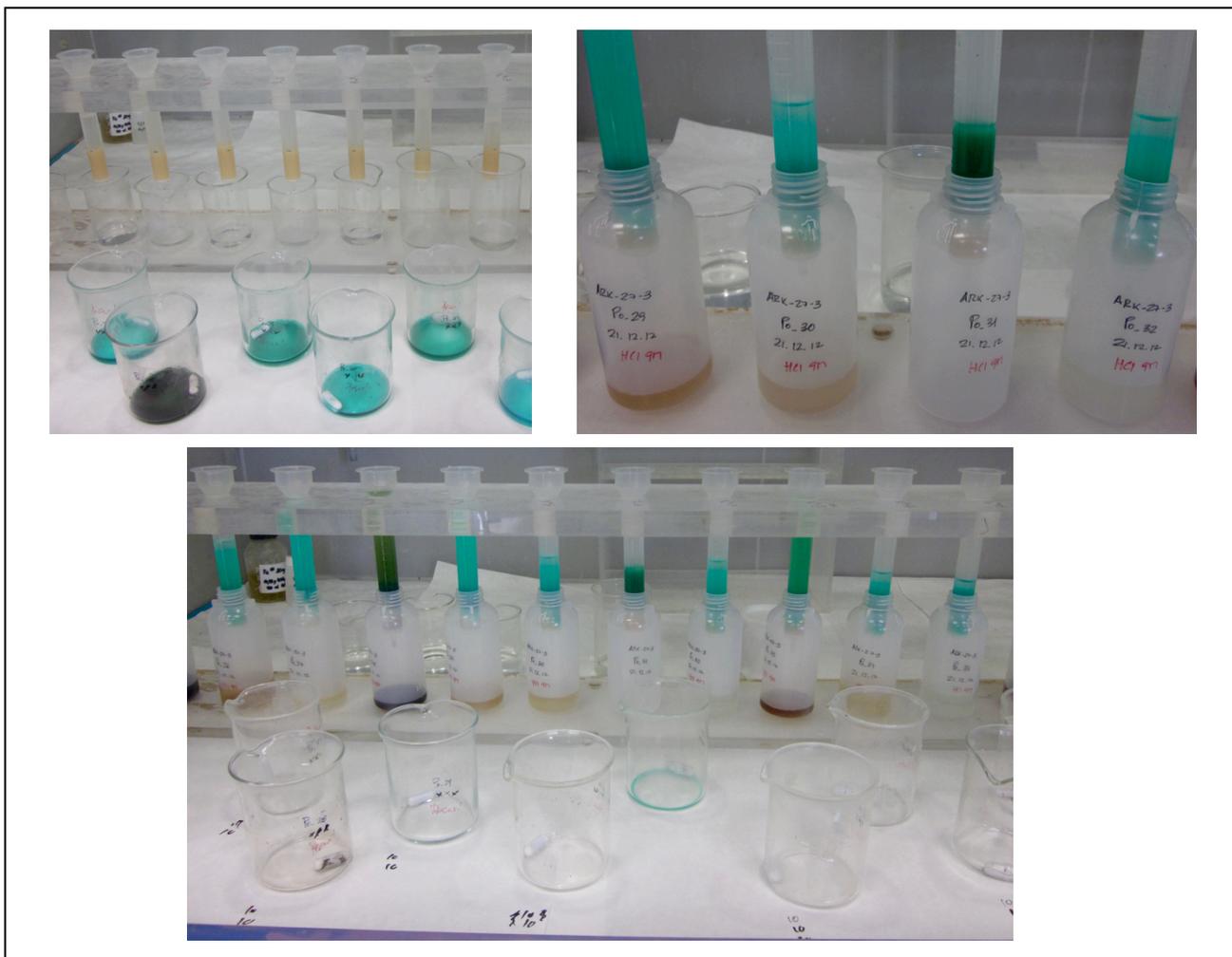


Image 4: Ion exchange columns. Effluents need to be stored for at least 6 months prior to re-plating.